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Additional inventors are being named on the _____ 1 _____ separately numbered sheets attached hereto					
TITLE OF THE INVENTION (500 characters max)					
Formation of a Reduced In-Situ Catalyst Complex Suitable for ATRP					
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[Page 1 of 2]

Respectfully submitted,

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[Page 2 of 2]

Number 1 of 1

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## Formation of a Reduced in-situ Catalyst Complex Suitable for ATRP

### Inventors

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### Field of the Invention

The present invention is directed to formation of a catalyst complex suitable for a controlled polymerization process, more directly related to a formation of an initiation system for a redox based controlled radical polymerization process wherein the catalyst complex is added to the reaction in the higher oxidation state and reduced to the activator state by addition of a reducing agent. The reduced catalyst complex interacts with a normal ATRP initiator molecule comprising one or more radically transferable atoms or groups to start the polymerization.

### Description of the Invention

ATRP is one of the most successful controlled/"living" radical processes (CRP) developed and has been thoroughly described in a series of co-assigned U.S Patents and Applications, U. S. Patent Nos. 5,763,546; 5,807,937; 5,789,487; 5,945,491; 6,111,022; 6,121,371; 6,124,411; 6,162,882; 6,407,187; 6,512,060; 6,538,091; 6,541,580; 6,624,262; 6,624,263 6,627,314;

and U.S. Patent Applications 09/359,359; 09/534,827; 09/972,056; 10/034,908; 10/289,545 and 10/456,324 all of which are herein incorporated by reference, and has been discussed in numerous publications by Matyjaszewski as co-author and reviewed in several publications.

A living polymerization process is a chain growth process without or with an insignificant amount of chain breaking reactions, such as transfer and termination reactions. Controlled/living polymerization, herein "controlled polymerization", is a chain growth process that under controlled polymerization conditions provides effective control over the chain growth process to enable synthesis of polymers with molecular weight control and narrow polydispersities or molecular weight distributions. Molecular weight control is provided by a process having a substantially linear growth in molecular weight of the polymer with monomer conversion accompanied by essentially linear semilogarithmic kinetic plots, in spite of any occurring terminations. Polymers from controlled polymerization processes typically have molecular weight distributions, characterized by the polydispersity index ("PDI"), of less than or equal to 2. The PDI is defined by the ratio of the weight average molecular weight to the number average molecular weight,  $M_w/M_n$ . More preferably in certain applications, polymers produced by controlled polymerization processes have a PDI of less than 1.5, and in certain embodiments, a PDI of less than 1.3 may be achieved.

Polymerization processes performed under controlled polymerizations conditions achieve these properties by consuming the initiator early in the polymerization process and, in at least one embodiment of controlled

polymerization, an exchange between an active growing chain and dormant polymer chain is equivalent to or faster than the propagation of the polymer. A controlled radical polymerization ("CRP") process is a process performed under controlled polymerization conditions with a chain growth process by a radical mechanism, such as, but not limited to, atom transfer radical polymerization, stable free radical polymerization, specifically, nitroxide mediated polymerization, reversible addition-fragmentation transfer/degenerative transfer/catalytic chain transfer radical systems. A feature of controlled radical polymerizations is the existence of an equilibrium between active and dormant species. The exchange between the active and dormant species provides a slow chain growth relative to conventional radical polymerization, but all polymer chains grow at the same rate. Typically, the concentration of radicals is maintained low enough to minimize termination reactions. This exchange, under appropriate conditions, also allows the quantitative initiation early in the process necessary for synthesizing polymers with special architecture and functionality. CRP processes may not eliminate the chain breaking reactions, however, the chain breaking reactions are significantly reduced from conventional polymerization processes.

Polymers produced under controlled polymerization conditions have a degree of polymerization that may be determined from the ratio of the amount of consumed monomer to the initiator, a polydispersity close to a Poisson distribution and functionalized chain ends. The level of control attained in a particular polymerization process is typically monitored by analyzing the kinetics

of the polymerizations, the evolution of molecular weights, polydispersities and functionalities with conversion.

The equilibrium required for ATRP controlled polymerization processes has been attained using three different initiation methods or activation reactions called respectively, normal ATRP, "reverse" ATRP and simultaneous normal and reverse initiation (SR&NI) ATRP. See U.S. Patent 5,763,548 and US Patent Application No. 10/271,025 for examples of these three initiation processes. We now describe a new non free radical initiator based reverse ATRP that overcomes the limitations of the three earlier procedures for initiation of ATRP.

In an ATRP process a transition metal complex participates in a repetitive redox reaction to homolytically remove a radically transferable atom or group from an initiator or growing chain end to form the active propagating radical species and then deactivates the growing chain end by donating back a transferable atom or group. In order to initiate the chain growth process the transition metal complex that acts as the catalyst for this repetitive addition process must be present, at least partially, in the lower oxidation state. However in order to act as a good catalyst the lower oxidation state must be readily oxidized which can introduce handling difficulties in large scale operations. The present process improvement allows the precursor of the catalyst complex to be added to the reaction in the oxidatively stable higher oxidation state and reduced to the active lower oxidation state by a non-radical forming reducing agent.



Overview and Definitions to be used herein or in conjunction with cited and incorporated references

It must be noted that, as used in this specification and the appended claims, the singular forms "a," "and," and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a polymer" includes more than one polymer, reference to "a substituent" includes more than one substituent.

Unless otherwise indicated, all numbers expressing quantities of ingredients, time, temperatures, and so forth used in the present specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, may inherently contain certain errors necessarily

resulting from the standard deviation found in their respective testing measurements.

Before describing the present invention in detail, it is to be understood that this invention is not limited to specific compositions, components or process steps, as such may vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting.

In describing and claiming the present invention, the following terminology will be used in accordance with the definitions set out below.

The term "polymer" is used to refer to a chemical compound that comprises linked monomers, and that may or may not be linear; in the context of the present invention, the "polymers", or segments of the polymers are, however, generally linear. Polymer "segments" refer to a polymer that is covalently bound to two additional moieties, generally end-capping moieties at each of two termini.

The term "alkyl" as used herein refers to a branched or unbranched saturated hydrocarbon group generally comprising 1 to 24 carbon atoms, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, t-butyl, octyl, decyl, tetradecyl, hexadecyl, eicosyl, tetracosyl and the like, as well as cycloalkyl groups such as cyclopentyl, cyclohexyl and the like. The term "lower alkyl" intends an alkyl group of one to six carbon atoms, preferably one to four carbon atoms.

The term "alkenyl" as used herein refers to a branched or unbranched hydrocarbon group generally comprising 2 to 24 carbon atoms and containing at least one double bond, typically containing one to six double bonds, more

typically one or two double bonds, e.g., ethenyl, n-propenyl, n-butenyl, octenyl, decenyl, and the like, as well as cycloalkenyl groups such as cyclopentenyl, cyclohexenyl and the like. The term "lower alkenyl" intends an alkenyl group of two to six carbon atoms, preferably two to four carbon atoms.

The term "alkylene" as used herein refers to a difunctional branched or unbranched saturated hydrocarbon group generally comprising 1 to 24 carbon atoms, such as methylene, ethylene, n-propylene, n-butylene, n-hexylene, decylene, tetradecylene, hexadecylene, and the like. The term "lower alkylene" refers to an alkylene group of one to six carbon atoms, preferably one to four carbon atoms.

The term "alkenylene" as used herein refers to a difunctional branched or unbranched hydrocarbon group generally comprising 2 to 24 carbon atoms and containing at least one double bond, such as ethenylene, n-propenylene, n-butenylene, n-hexenylene, and the like. The term "lower alkenylene" refers to an alkenylene group of two to six carbon atoms, preferably two to four carbon atoms.

The term "alkoxy" as used herein refers to a substituent --O--R wherein R is alkyl as defined above. The term "lower alkoxy" refers to such a group wherein R is lower alkyl.

The term "aryl" as used herein, and unless otherwise specified, refers to an aromatic moiety containing one to five aromatic rings. For aryl groups containing more than one aromatic ring, the rings may be fused or linked. Aryl groups are optionally substituted with one or more inert, nonhydrogen substituents per ring; suitable "inert, nonhydrogen" substituents include, for

example, halo, haloalkyl (preferably halo-substituted lower alkyl), alkyl (preferably lower alkyl), alkenyl (preferably lower alkenyl), alkynyl (preferably lower alkynyl), alkoxy (preferably lower alkoxy), alkoxycarbonyl (preferably lower alkoxycarbonyl), carboxy, nitro, cyano and sulfonyl. Unless otherwise indicated, the term "aryl" is also intended to include heteroaromatic moieties, i.e., aromatic heterocycles. Generally the heteroatoms will be nitrogen, oxygen or sulfur.

The term "arylene" as used herein, and unless otherwise specified, refers to a bifunctional aromatic moiety containing one to five aromatic rings. Arylene groups are optionally substituted with one or more substituents per ring as set forth above for substitution of an "aryl" moiety.

The term "halo" is used in its conventional sense to refer to a chloro, bromo, fluoro or iodo substituent. In the compounds described and claimed herein, halo substituents are generally bromo, chloro or iodo, preferably bromo or chloro. The terms "haloalkyl," "haloaryl" (or "halogenated alkyl" or "halogenated aryl") refer to an alkyl or aryl group, respectively, in which at least one of the hydrogen atoms in the group has been replaced with a halogen atom.

The term "heterocyclic" refers to a five- or six-membered monocyclic structure or to an eight- to eleven-membered bicyclic heterocycle. The "heterocyclic" substituents herein may or may not be aromatic, i.e., they may be either heteroaryl or heterocycloalkyl. Each heterocycle consists of carbon atoms and from one to three, typically one or two, heteroatoms selected from the group consisting of nitrogen, oxygen and sulfur, typically nitrogen and/or oxygen. The

term "nonheterocyclic" as used herein refers to a compound that is not heterocyclic as just defined.

The term "hydrocarbyl" is used in its conventional sense to refer to a hydrocarbon group containing carbon and hydrogen, and may be aliphatic, alicyclic or aromatic, or may contain a combination of aliphatic, alicyclic and/or aromatic moieties. Aliphatic and alicyclic hydrocarbyl may be saturated or they may contain one or more unsaturated bonds, typically double bonds. The hydrocarbyl substituents herein generally contain 1 to 20 carbon atoms, and may be substituted with various substituents and functional groups.

The term "hydrocarbylene" as used herein refers to a difunctional branched or unbranched saturated hydrocarbon group, typically containing 1 to 20 carbon atoms.

The term "inert" to refer to a substituent or compound means that the substituent or compound will not undergo modification either (1) in the presence of reagents that will likely contact the substituent or compound, or (2) under conditions that the substituent or compound will likely be subjected to (e.g., chemical processing carried out subsequent to attachment an "inert" moiety to a substrate surface).

The term "available" to refer to an optionally substituted carbon atom refers to a carbon atom that is covalently bound to one or more hydrogen atoms that can be replaced by a designated substituent without disrupting or destabilizing the remaining structure of the molecule.

"Optional" or "optionally" means that the subsequently described circumstance may or may not occur, so that the description includes instances where the circumstance occurs and instances where it does not. For example, the phrase "optionally substituted" means that a non-hydrogen substituent may or may not be present, and, thus, the description includes structures wherein a non-hydrogen substituent is present and structures wherein a non-hydrogen substituent is not present

#### Normal ATRP Initiation

Normal ATRP processes are initiated by the redox reaction between an added initiator comprising a transferable atom or group and catalyst comprising a transition metal complex in a lower oxidation state. A redox reaction occurs between the initiator and the transition metal complex. The transferable atom or group is an atom or group that may be homolytically cleaved from an initiator by the catalyst, thereby oxidizing the catalyst to a higher oxidation state and forming an active radical thereby activating the initiator residue for monomer addition. After initiation, an ATRP process, generally, is based a dynamic equilibrium between a transition metal complex reversibly activating and deactivating the polymer chain via a similar homolytic atom or group transfer via a redox reaction. Prior to monomer addition, the polymer chain is activated by the removal of a transferable atom or group from the end of the polymer chain and may then be deactivated by return of a transferable atom or group in the reverse reaction, the returning atom or group may not necessarily

be the same atom or group removed in the activating step or even from the same transition metal complex. The equilibrium between the growing and dormant chains allows the synthesis of well-defined polymers with complex architecture. During the dynamic equilibrium the transition metal complex cycles between a lower oxidation state and a higher oxidation state.

The advantages of normal initiation of ATRP include that the added initiator molecule includes the transferable atom or group needed to terminate each polymer chain, therefore no additional transferable atoms or groups are required to be added by other components of the polymerization process in order to attain polymers with the desired topology and degree of polymerization at high conversion of monomer(s) to polymer. Therefore, only enough transition metal complex in the *lower* oxidation state that is needed to provide suitable catalytic activity to the process is directly added. By suitable catalytic activity, it is meant that the polymerization comprises an amount of catalyst needed to drive the reaction to a desired degree of polymerization in a time that allows appropriate heat control to allow for a controlled reaction.

The disadvantages of normal initiation of ATRP are that transition metal complexes in the lower oxidation state are less stable than the transition metal complex in the higher oxidation state and, typically without special handling procedures, have to be prepared at the time of reaction or stored under an inert atmosphere. Further, care has to be taken with the other reagents in the reaction to reduce the level of oxidants in the system to retain the desired active catalyst system, since if such termination reactions occur, the amount of catalyst in the

lower oxidation state may be reduced, thereby also reducing the rate of polymerization. Any transition metal complex capable of maintaining the dynamic equilibrium with the polymer chain may be used as the redox catalyst in ATRP, as discussed in the cited art, after consideration of oxidation states, complex formation with suitable ligands and redox potential of the resulting complex to provide a catalyst for the desired reaction. A wide variety of ligands have been developed to prepare transition metal catalyst complexes that display differing solubility, stability and activity. However, the embodiments of the present invention described herein exemplify the process by focusing on the use of copper as the transition metal and butyl acrylate as the monomer but, as described in the cited art, other transition metals can be used and a wide range of radically (co)polymerizable monomers can be polymerized. Indeed almost any radically (co)polymerizable monomer can be (co)polymerized by preparing a catalyst complex with appropriate solubility, stability and activity as taught in the cited references and the relevant art.

#### Reverse ATRP initiation

In reverse ATRP, as opposed to normal ATRP, the transferable atom or group begins as a counterion or ligand on the transition metal complex in the higher oxidation state. Generally, the higher oxidation state of a transition metal complex is the oxidatively more stable state of the complex and can often be stored in the presence of air. In a "reverse ATRP" the reaction is then initiated by a generation of a radical by known processes, such as, by decomposition of a



standard free radical initiator which may directly participate in a redox reaction with the transition metal forming the transition metal complex in the lower oxidation state, the activator state, and a molecule with a transferable atom suitable for initiation of an ATRP reaction or it may initiate a polymerization that is quickly deactivated by the transition metal complex in the higher oxidation state. In this regard, a reverse ATRP process allows for controlled polymerization starting from lower cost, more oxidatively stable Cu(II) complexes. However, reverse ATRP systems require high catalyst concentration in order to introduce the appropriate concentration of radically transferable atoms or groups to the reaction in order maintain a controlled polymerization and to attain polymers of the desired molecular weight at high conversion of monomer to polymer. Due to the high concentration of catalysts required in reverse ATRP processes, only transition metal complexes with lower catalytic activity, such as, catalysts comprising bipyridine type ligands have been successfully employed.

A standard free radical initiator is essentially the source of free radicals required to initiate the polymerization of the radically polymerizable monomers. The free radicals may be formed by thermal or photoinduced decomposition of the initiator or by a redox reaction with the initiator. Typical standard free radical initiators include, but are not limited to, dialkyl diazenes, including, azobis(isobutyronitrile) ("AIBN"), dimethyl 2,2'-azobisisobutyrate (MAIB), 1,1'-azobis(1-cyclohexanenitrile), 2,2'-azobis(2,4,4-trimethylpentane), and azobis-2,4-dimethylvaleronitrile, polymeric or oligomeric materials comprising azo, -N=N-, groups, peroxides such as acyl and diacyl peroxides, alkyl peroxides, dialkyl

peroxydicarbonates, hydroperoxides, peresters, and inorganic peroxides, benzoyl peroxide (BPO) or a peroxy acid such as peroxyacetic acid or peroxybenzoic acid, styrenes and acrylates. Standard commercial free radical initiators, such as V-044, that initiate radical polymerizations are typically generated by thermal or photochemical homolytic cleavage of covalent bonds to form the radicals.

Because a typical reverse ATRP process depends on the thermal decomposition of the standard free radical initiator, a further limitation of a reverse ATRP process has been the narrow operating temperature range required to ensure fast decomposition and rapid initiation of the process at low conversion of monomer to polymer to provide polymers with narrow molecular weight distribution.

ATRP catalysts vary in catalytic activity based upon the properties of the transition metal, the ligands and the temperature and polarity of the reaction medium, as well as other factors. More active catalytic systems are generally less oxidatively stable in their lower oxidation states, such as the Cu(I) complexes discussed herein to exemplify the processes. Such catalysts in their lower oxidation states may create handling problems. For instance, trace levels of oxygen should be removed from the system prior to addition of the catalyst in a lower oxidation state and the catalyst complex may not easily be prepared in advance of the polymerization process. Reverse initiation of ATRP, using more stable Cu(II) complexes in the initiating step, may be a convenient method to circumvent these handling problems. The preparation of oxidatively

stable, active catalyst precursors, will allow larger scale manufacture, storage and shipment of catalyst systems.

Unfortunately, the known reverse ATRP initiation methods are difficult to apply to controlled polymerization using highly active catalysts such as CuBr/Me<sub>6</sub>-TREN for the preparation of lower molecular weight polymers at lower temperatures, or lower degrees of polymerization. The concentration of the catalyst to be added to a reverse ATRP is also related to the amount of added initiator and the temperature at which the initiator undergoes rapid decomposition. Additionally, rapid decomposition of the initiator is required to ensure each polymer chain grows simultaneously to synthesize polymers with narrow molecular weight distribution. Since the first radicals are provided by normal radical initiators it is difficult to prepare homo-telechelic polymers or block and graft copolymers.

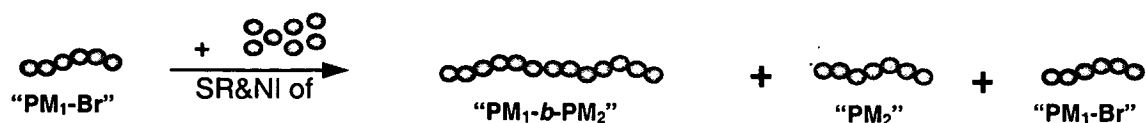
#### *SR&NI ATRP*

Accordingly simultaneous normal and reverse initiation was developed to allow the use of highly active ATRP catalysts in a reverse ATRP initiation process, see US Application 10/271,025. A SR&NI polymerization process comprises a dual initiation system for atom transfer radical polymerization ("ATRP"). The initiation system comprises both standard free radical initiators and initiators comprising a transferable atom or group. In certain embodiments the SR&NI initiation system comprises initiation of a reverse ATRP and normal ATRP process. The dual initiation system may be used to prepare

any type of polymer that may be prepared by ATRP, such as, but not limited to, homopolymers, graft, branched, star, comb, bottle brush, block copolymers, gradient, alternating, as well as other polymer structures. Additionally, the dual initiation system may be utilized in atom transfer radical polymerization processes conducted in bulk, in solution, in emulsion, in miniemulsion, and in heterogeneous polymerizations from surfaces. Indeed SR&NI may be particularly suited for polymerizations from surfaces since all the normal ATRP initiator molecules can be attached to the surface and the reverse activation of the transition metal complex can occur in the contacting reacting solution thereby providing attached polymers and, as discussed below, any homopolymer formed in the reaction remains in solution and readily removable.

There are however even limitations to the disclosed SR&NI ATRP process. Since a standard free radical initiator is added to the polymerization process to form radicals that reduce the stable catalyst complex to form the active catalyst complex this results in the formation of a low concentration of chains that are initiated by these radicals. This is shown in scheme 1 where a macroinitiator is used to form a block copolymer in the “normal” initiated ATRP but the radical initiator added to form the active catalyst complex in a “reverse ATRP” forms a homopolymer. A similar loss of complete control over functionality and topology would result from a SR&NI ATRP comprising the addition of a normal ATRP initiator with an attached functional group in conjunction with a standard radical initiator which would lead to preparation of polymers with reduced homo-telechelic functionality.

Scheme 1.



When the product of such a reaction is analyzed using 2-D Chromatography (LA-CC + SEC), see figures 1 and 2, it is clear that there is a significant amount of homopolymer present, 12% in a bulk SR&NI ATRP and 4.5% in the miniemulsion system in the provided examples. More active catalysts can provide lower levels of homopolymer, but some will always be present. For many applications such dilution of one phase of a block copolymer by a compatible homopolymer is acceptable, particularly when the molecular weight of the homopolymer is the same as the attached block, but for other applications a pure block copolymer or formation of a telechelic linear polymer with high functionality is desired. When high tele-functionality or high block copolymer purity is desired this would seem to require use of a normal ATRP process with the obligatory care to be taken over the preparation reaction components and addition of the catalyst complex.

Quite unexpectedly when we examined a series of experiments directed at conducting a simultaneous dual mechanism ring opening polymerization of  $\epsilon$ -caprolactam and ATRP of octadecyl methacrylate we concluded it might be possible to form a reduced catalyst complex from the oxidatively stable higher oxidation state metal complex without use of a standard free radical initiator. This concept involves use non-radical based chemistry to reduce the oxidatively

stable catalyst complex in the reaction medium. This can be accomplished by addition of inorganic reagents or organic reagents. The first option will be exemplified by defining conditions that allow addition of stannous oxalate or sodium sulfite to the reaction and the second by addition of ascorbic acid to a higher oxidation state catalyst complex to prepare high purity block copolymers. The possibility of the suitability of ascorbic acid as a potential reducing agent was described in a series of experiments designed to examine causes of damage to DNA it was found that cupric salts in the presence of ascorbic acid or mercaptoethanol can cause damage. It was proposed that ascorbic acid was oxidized by the cupric salts forming radical intermediates, [Sinohara, K. *Nippon Kagaku Kaishi* (1921-47) **1940**, 61, 733-740.] the copper being reduced to Cu(I). [Sinohara, K. *Nippon Kagaku Kaishi* (1921-47) **1940**, 61, 733-740 and Doadrio, A.; Arroyo, M. *Anales Real Soc. Espan. Fis. Quim. (Madrid) Ser. B.* **1966**, 62, 317-327.] However in these examples the target reaction examined was oxidation of ascorbic acid not preparation of copper based catalyst systems and no analysis of the reduced copper complex was undertaken and no effort was made to confirm the presence of radical intermediates, which would not be desired in the present application, and indeed would teach against the use of ascorbic acid in the present disclosed process.

There is one reference to the use of reducing sugars in ATRP by Klumpermann et.al. [de Vries, A.; Klumperman, B.; de Wet-Roos, D.; Sanderson, R. D. *Macromol. Chem. Phys.* **2001**, 202, 1645-1648.] They examined the effect of various reducing monosaccharides on the rate of atom transfer radical

polymerization of butyl methacrylate and reported that the addition of reducing sugars affects the rate of propagation in an ATRP with a 100% increase in the rate of polymerization in some cases. They indicated that a possible explanation for these observations is the ability of the reducing sugars to reduce part of the  $\text{Cu}^{2+}$  species, which deactivate the growing radicals, to  $\text{Cu}^+$ , thereby ensuring a shift in the equilibrium between active and dormant chains in the direction of the former with a resulting increase in the rate of reaction. They did not suggest that this reaction could be used to reduce all of the deactivator in the reaction since

They pointed out their system was completely controlled and that these organic reducing agents have little effect on the molecular weight and molecular weight distribution of the formed poly(butyl methacrylate) and that the polymers had polydispersity indexes that remained well below 1.2. Probably, because of the low solubility of these reagents, they do not significantly interact with the catalyst and cannot form side products (complexes) with it. In addition, the reducing activity is at least partially decreased by the low solubility, and that is why the application of these sugars was successful to increase the propagation rate.

Early experiments with ascorbic acid and sodium sulfite as reducing agents in mini-emulsion polymerization polymerizations now indicates the system was viable for reducing the  $\text{Cu(II)}$  copper complex to form an active catalyst system but that the concentration of the reducing agent in the reaction medium, the oil phase, has to be well controlled. At the time of the first experiments the lack of control was not seen as an opportunity to form a new process for initiation

of an ATRP reaction now with this as an objective this could be accomplished by addition of a phase transfer agent or an oil soluble reducing agent.

Once conditions for use of a non-radical reducing agent for formation of a catalytically active transition metal complex in its activator state are defined the new initiation system may be used to prepare any type of polymer that may be prepared by ATRP, such as, but not limited to, homopolymers, graft, branched, star, comb, bottle brush, block copolymers, gradient, alternating, as well as other polymer structures. Additionally, the initiation system may be utilized in atom transfer radical polymerization processes conducted in bulk, in solution, in emulsion, in miniemulsion, and in heterogeneous polymerizations from surfaces. One requirement for the disclosed initiation system is that the oxidatively stable transition metal complex is reduced to the desired degree by a non-radical forming reducing agent and that the reducing agent that does interact with the radically transferable atom or group on the higher oxidation state transition metal complex forms a molecule comprising a species from which the radically transferable atom can not be abstracted by the lower oxidation state transition metal catalyst complex. Once such conditions are identified then the reduction reaction can be conducted in-situ or prior to addition of the catalyst complex to the reaction medium. In this way a normal ATRP reaction is catalyzed by activation of the deactivator by a non-radical, or non-ATRP initiating, reduction reaction. This procedure has all the benefits of a normal ATRP initiated polymerization plus the benefits, or freedom, of adding the catalyst complex to the reaction medium in its more stable higher oxidation state.



The features and advantages of the present invention may be better understood by reference to the accompanying figures, in which:

Figure 1, shows the characterization of a tri-arm block copolymer formed in a bulk copolymerization using SR&NI.

Figure 2, shows the characterization of a tri-arm block copolymer formed in a miniemulsion polymerization process with SR&NI using a more active catalyst complex.

Figure 3, kinetics of a one pot reaction dual mechanism copolymerization of caprolactam and octadecyl methacrylate.

Figure 4, the GPC traces for simultaneous copolymerization of caprolactam and octadecyl methacrylate.

Figure 5, kinetics of a one pot reaction dual mechanism copolymerization of caprolactam and octadecyl methacrylate starting from Cu(II) complex reduced in-situ with tin ocatanoate.

Figure 6, the GPC traces for simultaneous copolymerization of caprolactam and octadecyl methacrylate starting from Cu(II) complex reduced in-situ with tin ocatanoate.

The following series of examples show the need for the present invention and the experiments led to the processes to meet the need. This includes understanding

why some experiments that failed to meet their initial target can lead to a new concept. The net result is that a fourth approach to initiate an ATRP was developed, one that allows addition of an oxidatively stable catalyst complex that is activated in situ in the absence of free radical sources and hence without formation of a second ATRP initiator. This concept could be formation of a Reduced In-Situ Catalyst complex suitable for ATRP or RISC ATRP.

## Examples.

### 1. SR&NI (Comparison Runs)

Regarding the proposed mechanism of SR&NI ATRP, the resulting block copolymers would contain a few number of homopolymer chains, which were initiated by AIBN through a “reverse ATRP” process. However the majority are block copolymer chains, which initiated by macroinitiator through a normal ATRP process. To evaluate the composition of the resulting materials a block copolymerization was conducted and the composition of final product was analyzed by 2D chromatography.

#### a. SR&NI in a Bulk Copolymerization

In a typical batch polymerization,  $\text{CuBr}_2$  and ligand were degassed in a Schlenk flask by three nitrogen/vacuum cycles. Then, pre-deoxygenated monomer was added to the flask using previously purged syringes. The solution was stirred for 10-20 min at 60 °C to form the  $\text{Cu}^{\text{II}}$  complex in a homogenous solution. The pre-deoxygenated alkyl halide (i.e., MBP or EB/B) was injected to the flask under nitrogen atmosphere. The flask was immersed in an oil bath thermostated at 80 °C. The polymerization was initiated by the injection of pre-

deoxygenated AIBN in anisole solution using pre-purged syringe. Samples were withdrawn periodically to monitor the monomer conversion, copolymer composition, and molecular weight. Run ML143 was conducted to prepare a tri-arm poly(methyl acrylate) macroinitiator that was isolated and purified prior to chain extension in run ML144 (bulk).

Run	Sample	Stoichiometry	Conv.	$M_{n,th}$ (g/mol)	$M_{n,sec}$ (g/mol)	$M_w/M_n$
ML143	(PMA-Br) <sub>3</sub>	[MA]/[CuBr-PMDETA]/[TB/BPE] = 300/1/1	0.41	10,600	9,200	1.08
ML144	(PMA) <sub>3</sub> - <i>b</i> -(PS) <sub>3</sub>	[St]/[ML143]/[CuBr <sub>2</sub> -BPMODA]/[AIBN] = 300/1/0.6/0.375	--	--	30,100	1.32

The result of 2-D chromatography of the polymer prepared in Run ML 144 is shown in Figure 1. The final product had 12% homo-polystyrene present in the material.

#### b. SR&NI in a Mini-emulsion system

The radical deactivator (CuBr<sub>2</sub> and ligand), monomer, and costablizer (hexadecane) were charged in a round-bottom flask, and heated with magnetic stirring at 60 °C for 10-20 minutes to form a homogenous solution. After cooling down to room temperature, AIBN was charged with stirring. Then, the surfactant solution was added and the mixture was ultrasonified (Heat Systems Ultrasonics W-385 sonicator; output control at 8 and duty cycle at 70% for 1 minutes) in an ice bath to prevent a significant temperature rise resulting from sonification. After homogenization, the miniemulsion was transferred to a 25 ml Schlenk flask, where pure argon was bubbled through the miniemulsion for 30 minutes before it

was immersed in an oil bath thermostated at 80 °C. The magnetic stirring speed was set at 700 rpm. Time zero of the polymerization was marked when the Schlenk flask was immersed in the oil bath. Samples were withdrawn periodically via pre-degassed syringe to monitor the monomer conversion, copolymer composition and molecular weight.

Conditions for the synthesis of water-borne 3-arm poly(*n*-butyl acrylate) in a miniemulsion system via a simultaneous reverse and normal initiation in ATRP process are shown below.

Run	Sample	Stoichiometry	Conv.	$M_{n,th}$ (g/mol)	$M_{n,sec}$ (g/mol)	$M_w/M_n$
ML145*	(PMA) <sub>3</sub> - <i>b</i> -(PS) <sub>3</sub>	[St]/[ML143]/[CuBr <sub>2</sub> -BPMODA]/[AIBN] = 300/1/0.6/0.375	0.93	27,300	22,100	1.37

Miniemulsion system: [Brij 98]/[hexadecane] = 2.3/3.6 wt% based on monomer; solid content = 20 % (based on 100% conversion).

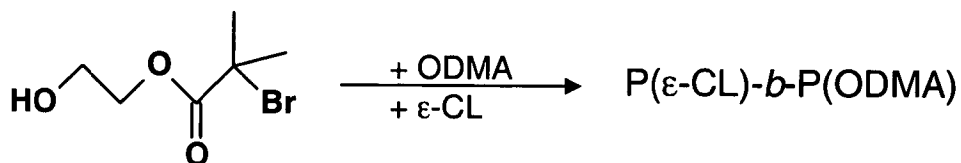
The results of the 2-D chromatography analysis for run ML143 is shown in Figure

2. The final product had 4.5% styrene present in the material.

## 2. Identification of ability of stannous oxalate to reduce cupric complexes

### a. Simultaneous copolymerization of caprolactam and octadecyl methacrylate (Comparison Run)

Initial dual process copolymerization: Conducting an atom transfer radical polymerization (ATRP) and anionic ring opening polymerization (AROP) in the same time:



The catalyst for AROP of  $\epsilon$ -caprolactam (CL) was tin(II) ethylhexanoate and the catalyst for ATRP of octadecyl methacrylate (ODMA) was CuCl/d-n-bipy. The polymer was characterized by NMR and proved simultaneous polymerization occurred. The kinetics of this process was followed by GPC providing the MW and PDI of the copolymer and conversion of ODMA as the polymerization progressed. The kinetics of the polymerization of CL was obtained by using GC to follow the reaction.

The reaction conditions for run identified as WJ 70 were addition of  $\epsilon$ -caprolactam (sufficient monomer to target a DP of 85) and octadecyl methacrylate (sufficient monomer to target a DP of 30) were added to a Schlenk flask followed by toluene (same volume as  $\epsilon$ -caprolactam) di-n-bpy (0.5 equivalents with respect to ODMA) and cuprous chloride (0.5 equivalents with respect to ODMA). The flask was purged of oxygen by bubbling with nitrogen then tin octanoate (3 equivalents with respect to  $\epsilon$ -caprolactam) and hydroxyl ethyl 2-bromoisobutyrate (1 equivalent with respect to ODMA), were added. The reaction was immersed in an oil bath and stirred at 75 °C. The results are presented in Table 1 and Figure 3.

GC measurement for CL: analysis was carried out isothermally at 40 °C for 2 min followed by an increase of temperature to 200 °C at the heating rate of 40 °C/min and holding at 200 °C for 4 min. The conversion was calculated by detecting the decrease of CL peak area relative to the peak area of the toluene.

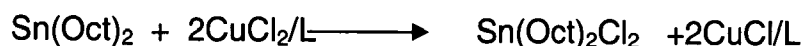
Table 1. Results or Run WJ 70

Time [min]	conv. ODMA	conv. CL	Mw	PDI
0	0	0	0	0
50	0.902	0	16700	1.27
93	0.913	0.201	17900	1.30
145	0.921	0.309	20300	1.28
250	0.927	0.597	26700	1.25
360	0.934	0.853	27300	1.25
1020	-	-	28600	1.34

Polymerization of ODMA is much faster than the anionic ring opening polymerization of CL. After 50 min conversion of ODMA reached 90% when CL less than 5%. GPC result (Figure 4) shows low polydispersity for the resulting copolymer, PDI=1.34, and higher  $M_w = 28600$  than theoretical  $M_{\text{theory}} = 20000$  (for 100% of conversion of both monomers). This difference may occur due to much more different hydrodynamic volume of copolymer and PMMA, which was a standard for calibrating GPC.

**b. Addition of Cupric complexes to dual mechanism copolymerization.  
(Identification of role of tin octanoate)**

The conditions employed for this reaction were selected to try to slow down the ATRP of ODMA and accelerate AROP of CL. Since the rate of the ATRP process was faster than the AROP process copper(II) was added to the system in an effort to achieve the same rate of both ATRP and AROP. Run WJ 77, was run under the similar conditions to run WJ 70 except that 0.18 equivalents of cupric chloride and an additional 0.18 equivalents of di-n-bpy were added to the reaction, (these steps should deactivate the rate of polymerization of ODMA by a factor of ten). Further the reaction was heated to 90 °C to increase the rate of AROP of CL. It did not slow down the ATRP of ODMA. The opposite effect was observed; an acceleration of the ATRP polymerization occurred. The reason of this behavior is shown below:



Copper (II) may react with tin(II) catalyst and produce tin(IV) and copper(I) which will accelerate the polymerization of ODMA.

In reaction WJ 78 the same conditions as WJ 77 were employed but without tin(II) catalyst. The color of the solution changed from dark brown to green in 20 minutes. The reaction was continued for 20h and as shown in Table

2 no polymerization occurred during this time. After this period of time tin catalyst was added and the color of the reaction solution immediately turned brown and polymerization took place. This is the best indication that a reaction between Sn(II) and Cu(II) occurred producing Sn(IV) and Cu(I) and that the Cu(I) can activate an ATRP.

Table 2		WJ 78			
	Time [min]	conv. ODMA	conv. CL	Mw	PDI
	0	0	0	-	-
	20	0	0	-	-
	50	0	0	-	-
	160	0	0	-	-
+ tin catalyst →	240	0	0	-	-
	1200	-	-	4600	1.12
	1350	-	-	19400	2.20
	1430	-	-	22500	1.87
	1710	-	-	27800	1.61

**c. ATRP accomplished by activation of a cupric halide complex with tin octanoate.**

In this run the ATRP catalyst was added as the cupric complex. Run (WJ 95) Target DP for CL = 95; Target DP for ODMA = 30; Normal ATRP initiator hydroxyl ethyl 2-bromoisobutyrate (1 equivalent); ATRP catalyst complex CuCl<sub>2</sub> (0.15 equivalents); Ligand di-n-bpy (0.15 equivalents); ROP catalyst tin(II) ethylhexanoate; Solvent toluene (1 equivalent to CL); Temperature 90 °C. The results are shown in Table 3 and in Figures 5 and 6.

Table 3		WJ 95			
	Time [min]	conv. ODMA	conv. CL	Mw	PDI
	0.0000	0	0	0.0000	0
	20.000	0.76	0.05	13700	1.30
	50.000	0.85	0.10	15700	1.30
	110.00	0.88	0.66	22300	1.24
	180.00	0.92	0.90	24200	1.24
	360.00	0.95	0.91	24000	1.26

It is clearly seen that polymerization of both monomers occurred and that the ATRP of ODMA occurred just as rapidly as in the first comparison run, WJ 70. Figure 6 shows that a block copolymer with narrow molecular weight distribution was prepared; i.e. both polymerization mechanism were well controlled. This indicates that tin octanoate can act to reduce a cupric halide complex to a Cu(I) state and that this formed complex can activate an ATRP from an added alkylhalide initiator and that remaining tin octanoate can initiate the ROP of caprolactam.

### **3. Identification and use of Ascorbic acid as a reducing agent for cupric complexes.**

#### **a. Reduced in-situ Catalyst (RISC) ATRP of Styrene Using Ascorbic Acid**

Run DST-26: ST/CuBr<sub>2</sub>/EBIB/PMDETA/Ascorbic acid = 100/1/1/1/0.475

CuBr<sub>2</sub> = 0.0975 g ( $0.4364 \times 10^{-3}$  mol); PMDETA = 0.091 ml (0.0757g = 0.

$4364 \times 10^{-3}$  mol); Styrene = 5 ml (4.545g =  $43.64 \times 10^{-3}$  mol); Toluene = 0.5 ml;

EBIB = 0.064 ml (0.085g =  $0.4364 \times 10^{-3}$  mol); Ascorbic Acid = 0.0365 g

( $0.2073 \times 10^{-3}$  mol). Reaction Temperature T=90 °C



The reaction underwent immediate initiation and conversion of styrene increased linearly with time. There was a clean shift in the GPC traces of samples taken throughout the reaction to higher molecular weight.

#### **4. Addition of a water soluble reducing agent to Cu(II) in a miniemulsion ATRP**

##### **a. Emulsion polymerization of n-BuMA by direct ATRP in the presence of ascorbic acid as reducing agent (nvt-buma 7)**

It would be convenient to carry out polymerizations by ATRP without purging the monomer, solvents, &c. with inert gas in order to remove oxygen. Ascorbic acid is known as a very efficient reducing agent for copper (II) ions, which are reduced to copper (I). It also reduces oxygen, especially in the presence of copper ions. That is why it seemed reasonable to try to use ascorbic acid dissolved in one phase (aqueous), in which it could be in contact only with copper (II) species, and the polymerization and generation of radicals to take place in another phase (oil, i.e. monomer phase). Emulsion polymerization seemed to be the best method in this respect. The experiment was carried out as follows. Emulsion from 0,0068 g ( $4,74 \cdot 10^{-5}$  mol) copper (I) bromide, 0,0382 g ( $9,35 \cdot 10^{-5}$  mol) dNBpy dissolved in 1.5 ml (1.341 g; 9.43 mmol) n-BuMA and 0.205 g Brij 98 and 0.0180 g (0.1 mmol) ascorbic acid dissolved in 10 ml water was prepared. The monomer and water used were not degassed previously. The mixture was not degassed. The Schlenk flask with the so prepared emulsion was put in an oil bath at 90°C (stirring). To this, 6.9 µl (0.0092 g  $4.7 \cdot 10^{-5}$  mol) ethyl

bromo-isobutyrate was added. Immediately a sample for GC was taken. At certain times, samples were taken again. The conversions were determined by GC and gravimetrically. Molecular weights of the polymers were determined with 1,4-dimethoxybenzene internal standard in THF. After 4 hours of stirring the mixture became green.

**Table 4.** Characteristics of the polymers prepared in experiment nvt-buma 7

Sample	Time of Polymerization, h	Conv. (GC)	$M_n \cdot 10^{-4}$	PDI
Buma 7-1	1	0.0429	1.348	2.926
Buma 7-2	2	0.0753	2.011	5.085
Buma 7-3	3	0.0780	1.408	3.811
Buma 7-4	4	0.5365	0.7086	6.286

From the above results it is seen that the polymerization is not controlled; ascorbic acid acts as inhibitor at the beginning, and when it is consumed (oxidation by the oxygen in the flask), the polymerization becomes very fast. This experiment was unsuccessful also probably due to the very fast and continuous reduction reaction of copper (II) by ascorbic acid; at these conditions no deactivator exists in the system. The experiment will be repeated later at different conditions.

**b. Emulsion polymerization of n-BuMA by direct ATRP in the presence of sodium sulfite as reducing agent (nvt-buma 8)**

Another reducing agent for copper (II), which is not oil (i.e. monomer) soluble, is sodium sulfite. As it is alkaline, it should be used in the presence of a little amount of acid. This makes the system very complicated. The experiment was unsuccessful as the polymerization was extremely fast (more than 75 % conversion for 10 minutes). The experiment was carried out as follows. Emulsion from 0,0071 g ( $4.95 \times 10^{-5}$  mol) copper (I) bromide, 0,0382 g ( $9,35 \cdot 10^{-5}$  mol) dNBpy, and 0.2 ml  $C_{16}$  dissolved in 1.5 ml (1.341 g; 9.43 mmol) n-BuMA and 0.199 g Brij 98 and 0.0390 g (0.31 mmol) sodium sulfite dissolved in 10 ml water was prepared. The monomer and water used were not degassed before the experiment. The mixture was not degassed. The Schlenk flask with the emulsion was put in an oil bath at 90°C (stirring). To this, 0.1 ml acetic acid and 6.9  $\mu$ l (0.0092 g  $4.7 \times 10^{-5}$  mol) ethyl bromo-isobutyrate was added. The mixture became brown immediately. A polymer started to separate and in 10 minutes a large quantity of polymer separated and the polymerization was stopped. This polymer, after washing with methanol and drying weighed 1.002 g (more than 75 % conversion).

These results show the importance of adding only the appropriate amount of reducing agent to reduce the required/desired amount of Cu(II) to Cu(I). An excess of reducing agent should be avoided since the deactivator (Cu(II)) needs to be present throughout the polymerization to control the ATRP reaction.

Results to be added when available from Ke.

Claims.

1. A polymerization process, comprising:

polymerizing free radically polymerizable monomers in the presence of a system initially comprising:

a catalyst comprising a transition metal compound in a higher oxidation state, wherein the transition metal compound when present in its lower oxidation state is capable of participating in a redox reaction with an initiator or dormant chain end comprising a radically transferable atom or group, and

a ligand that forms an active complex with the transition metal compound;

and

a reducing agent.

2. The polymerization process of claim 1, wherein the reducing agent is a non radical forming metal complex.

3. The polymerization process of claim 1, wherein the reducing agent is a non radical forming organic molecule.

4. The polymerization process of claim 1, wherein the polymerization process is one of a bulk polymerization, conducted in a solvent, an emulsion, mini-emulsion polymerization process, and a biphasic process wherein at least one of the initiators is attached to a substrate.
5. The polymerization process of claim 1, wherein the initiator comprising the transferable atom or group is attached to a solid surface.
6. The polymerization process of claim 5, wherein the solid surface is at least one of a flat surface or a curved surface.
7. A polymerization process for forming a polymer emulsion, mini-emulsion or suspension, comprising:
  - polymerizing one or more radically polymerizable monomers in the presence of a system initially comprising:
    - a suspending medium;
    - a surfactant;
    - a monomer phase suspended in the suspending medium,
  - wherein the monomer phase comprises at least a portion of the monomers,
  - an initiator comprising a transferable atom or group;
  - a reducing agent; and

a catalyst comprising a transition metal compound in a higher oxidation state, wherein the transition metal compound is capable of participating in a redox reaction, and  
a ligand that forms an active complex with the transition metal compound.

8. The polymerization process of claim 7, wherein the suspending medium is an inorganic liquid.

9. The polymerization process of claim 8, wherein the suspending medium is water.

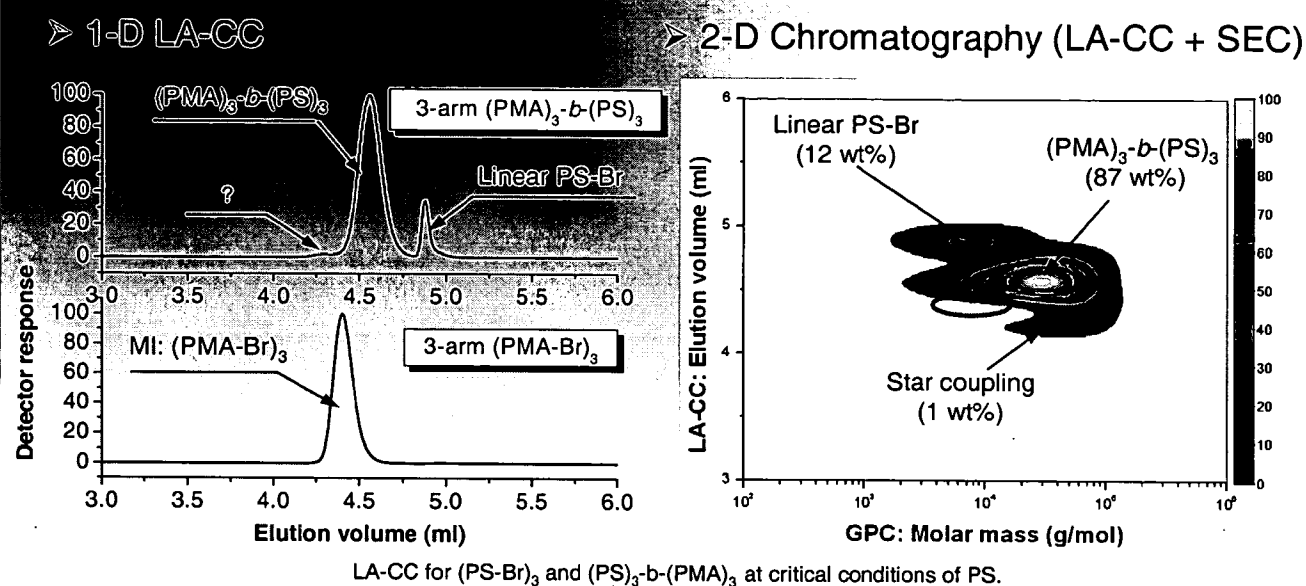
10. The polymerization process of claim 7, wherein the reducing agent is water soluble.

11. The polymerization process of claim 7, wherein the reducing agent is soluble in the suspended reaction medium.

12. The polymerization process of claim 7, wherein the initiator comprising a transferable atom or group is at least one of an alkyl halide and substituted esters.

13. The polymerization process of claim 7, wherein the catalyst is involved in a redox reaction between a higher oxidation state and a lower oxidation state.

# Characterization of 3-Arm Block Copolymer — $(\text{PMA})_3\text{-}b\text{-(PS)}_3$ (II)

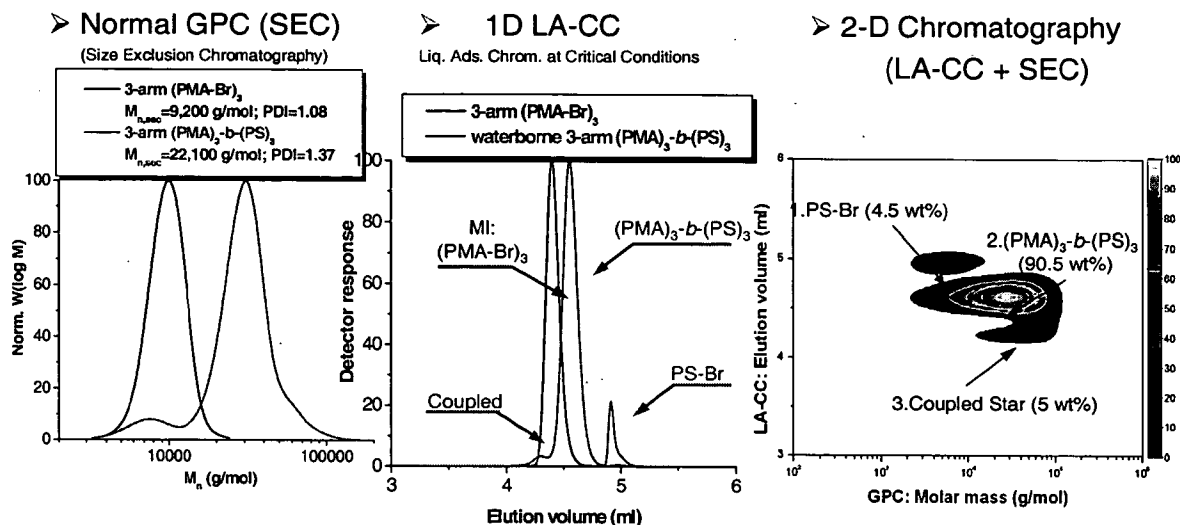


- ✓ 87% star copolymer; 12wt% linear PS-Br, 1wt% star coupling,  
and no residual  $(\text{PM})_3$  macroinitiator in final product

Figure 1. 2-D Chromatographic analysis of a tri-arm block copolymers prepared using SR&NI in a bulk copolymerization.

# Analysis of Waterborne 3-Arm Block Copolymer

## — (PMA)<sub>3</sub>-b-(PS)<sub>3</sub>



LA-CC for (PS-Br)<sub>3</sub> and (PS)<sub>3</sub>-b-(PMA)<sub>3</sub> at critical conditions of PS.

✓ ~4.5wt% PS-Br, 5wt% coupled star, no residual (PM)<sub>3</sub> macroinitiator in final product.

[St]<sub>0</sub>/[(PMA-Br)<sub>3</sub>]<sub>0</sub>/[CuBr<sub>2</sub>/BPMODA]<sub>0</sub>/[AIBN]<sub>0</sub> = 300/1/0.6/0.375 (100/1/0.2/0.125 for each arm); 80 °C.

Brij 98/hexadecane = 2.3/3.6 wt% based on monomer; 20% solid.

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Figure 2. 2-D Chromatographic analysis of a tri-arm block copolymers prepared using SR&NI in a mini-emulsion copolymerization.



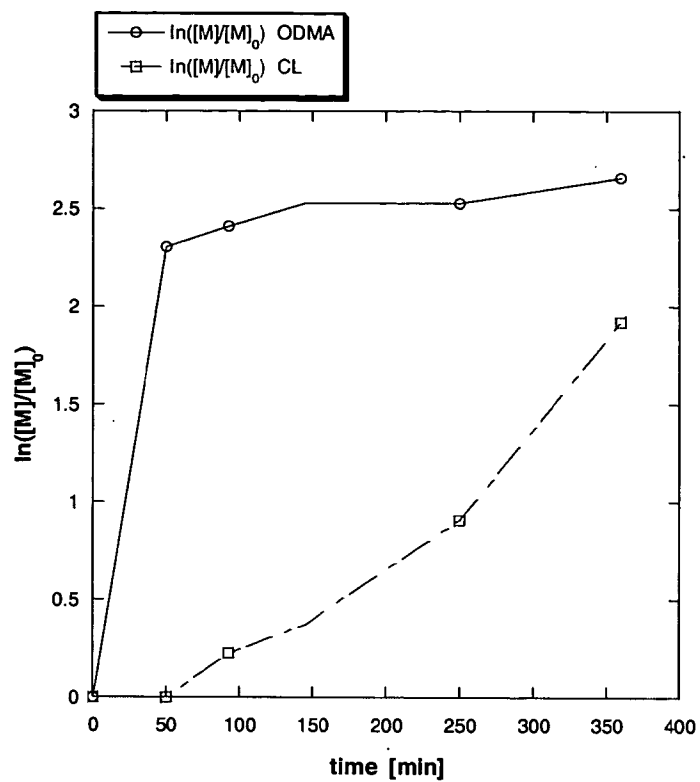


Figure 3. Kinetics of one pot reaction CL and ODMA

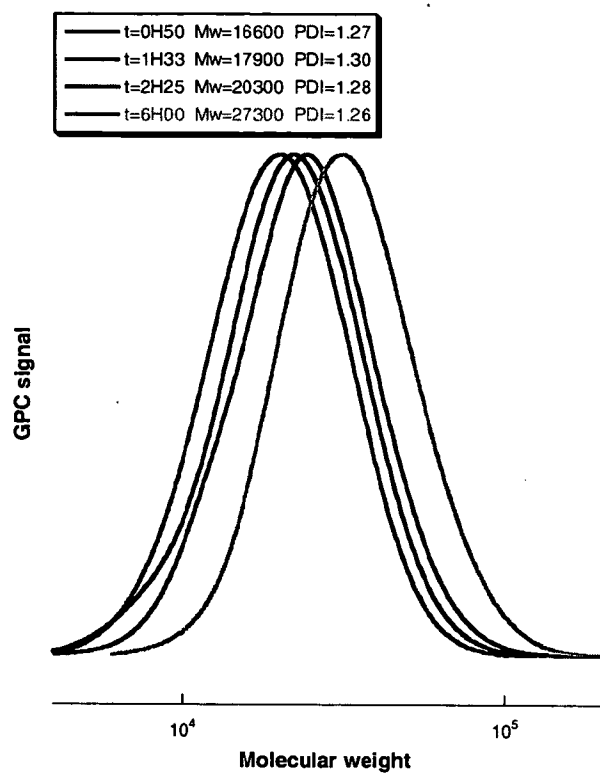


Figure 4. The GPC traces for simultaneous copolymerization of CL and ODMA

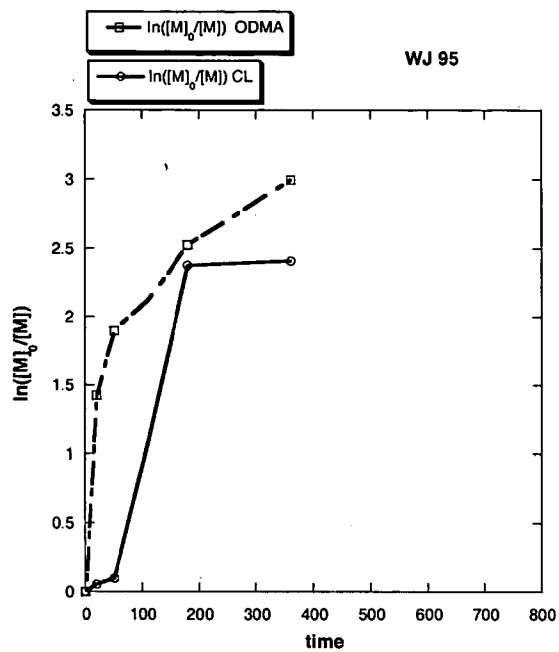


Figure 5

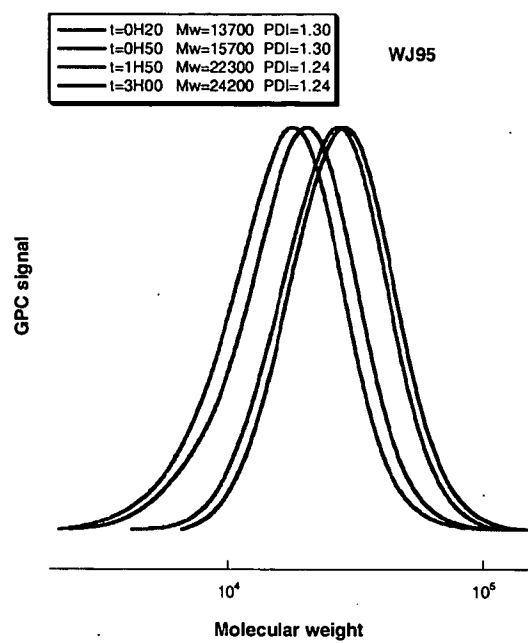


Figure 6